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Reactions of cycloalkanecarboxylic acids with SF_4. III. Fluorination of cyclobutane- and cyclopentane-tetracarboxylic acids with SF_4★

Yu.M. Pustovit, P.I. Ogojko, V.P. Nazaretian*

The Ukrainian Academy of Sciences, Institute of Organic Chemistry, Kiev 252094, Ukraine

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Abstract

Fluorination of cyclobutane- and cyclopentane-polycarboxylic acids having carboxylic groups in *cis* positions with SF_4 yields mainly cyclization products, i.e. cyclic $\alpha,\alpha,\alpha',\alpha'$-tetrafluoroethers. 1,3-Cyclization was observed during fluorination of cyclopentanetetracarboxylic acids.

Keywords: Cycloalkanecarboxylic acids; Sulphur tetrafluoride; Cyclization; Stereochemistry; NMR spectroscopy

1. Introduction

The formation of cyclic $\alpha,\alpha,\alpha',\alpha'$-tetrafluoroethers during the fluorination of polycarboxylic acids with SF_4 is governed mainly by steric factors, i.e. by the mutual separation and spatial configuration of the carboxylic groups [1–3]. With acyclic polycarboxylic acids containing carboxylic groups at the 1,2- and 1,3-positions, the formation of the corresponding 5- and 6-member cyclic $\alpha,\alpha,\alpha',\alpha'$-tetrafluoroethers has been observed in low yield [4].

2. Experimental

^1H and ^{19}F NMR spectra were measured with a Bruker WP-200 NMR spectrometer using TMS and $CFCl_3$ as respective internal standards and acetone-d_6 as the solvent. Upfield ^{19}F chemical shift values are negative. Gas–liquid chromatography was carried out with a Chrom 5 chromatograph using FID and helium as the carrier gas. A stainless-steel column (2500×3 mm) filled with 10% polyphenylmethylsiloxane on Chromatone AW (0.20–0.25 mm) was employed. Preparative GLC was carried out with a PACHV 07 chromatograph fitted with a thermal conductivity detector, a stainless-steel column (2600×12 mm) filled with 10% polyphenylmethylsiloxane on Chromatone N-AW-HMDS (0.32–0.40 mm) being used with helium as the carrier gas. All boiling and melting points reported are uncorrected.

2.1. Treatment of carboxylic acids with SF_4. General procedure

An acid and SF_4 were reacted in a stainless-steel cylinder using the relevant amounts of reactant, reaction time and temperature as indicated in Table 1. The gaseous products were released and the liquid residue poured into ice/water. The organic layer was separated, dried over P_2O_5 and purified by distillation or preparative GLC, as necessary. The physical properties and

Table 1
Reactions of carboxylic acids with SF_4

Acid		SF_4 (mmol)	Reaction conditions		Reaction product(s), yield (%)
No.	mmol		Temperature (°C)	Time (h)	
1	50	418	145	7	**2**, 70; **3**, 8
4	13	198	90	7	**5**, 70
6	16	200	115	6	**7**, 86
8	50	550	115	8	**9**, 80; **10**, 15

★Dedicated to Professor L.M. Yagupolskii on the occasion of his 70th birthday.

*Corresponding author.

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analyses of the products are listed in Table 2 and the NMR spectral data in Table 3.

3,5-Bis(trifluoromethyl)-1,2-cis-2,3-trans-3,5-cis-cyclopentane-1,2-dicarboxylic acid (11)

A mixture of compounds **9** and **10** (4.3 g), obtained in the reaction of *trans,cis,trans*-cyclopentane-1,2,3,4-tetracarboxylic acid (**8**) with SF_4, was heated at 100 °C (4 h) in a sealed tube with 4.9 g of 6% oleum and then cooled to 195 K (Dry Ice). Water (1 cm^3) was added and the colourless precipitate which formed collected by filtration and recrystallized from water.

*3,5-Bis(trifluoromethyl)-1,2-trans-2,3-trans-3,5-*cis*-cyclopentane-1,2-dicarboxylic acid (12)*

3,5-Bis(trifluoromethyl)-1,2-*cis*-2,3-*trans*-3,5-*cis*-cyclopentane-1,2-dicarboxylic acid (**11**) and excess concentrated hydrochloric acid were heated at 200 °C (2 h) in a sealed tube. The ^{19}F NMR spectrum showed a 30% conversion of acid **11** to acid **12**.

cis-6,8-Bis(trifluoromethyl)-3-aza-transoid-bicyclo[3,3.0^{1,5}]octane-2,4-dione (13)

A solution consisting of 0.735 g (2.5 mmol) of compound **11** in ether was added to an excess of ether saturated with dry ammonia. The ammonium salt of **11** was collected by filtration and dried *in vacuo* at 100 °C. It was then heated at 185–200 °C (0.5 h) to allow cyclization. The residue was sublimed at 80–85 °C *in vacuo* (20 mmHg). Yield, 0.68 g (99%). Recrystallization of this product from benzene afforded **13** as colourless crystals.

3. Results and discussion

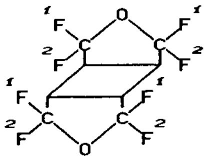
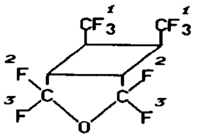
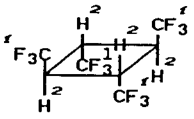
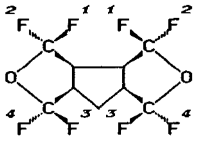
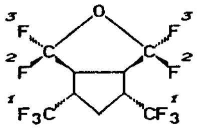
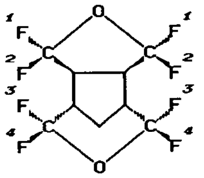
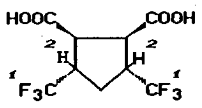
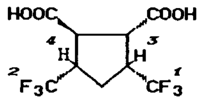
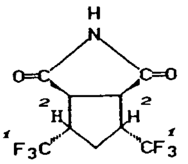
Fluorination of *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylic acid (**1**) with SF_4 under relatively forced conditions (7 h at 145 °C) yielded the tricyclic diether **2** as the main product together with smaller amounts of the bicyclic ether **3** (Scheme 1). The fully fluorinated product, *cis,trans,cis*-1,2,3,4-tetrakis(trifluoromethyl)cyclobutane was not formed.

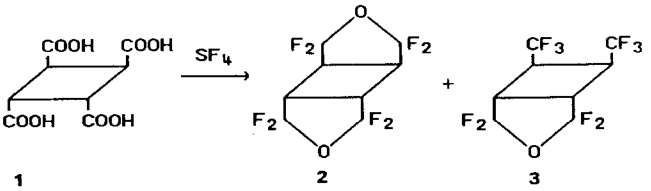
Fluorination of *trans,trans,trans*-1,2,3,4-cyclobutanetetracarboxylic acid (**4**), which was obtained by isomerization of acid **1** [5], when conducted at much lower

Table 2
Physical properties of compounds prepared

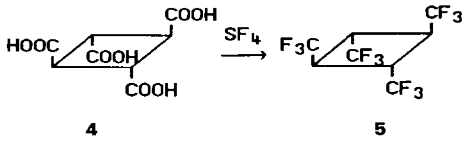
Compound No.	B.p./mmHg [m.p.] (°C)	d_4^{22} (g cm^{-3})	n_D^{22}	Elemental analyses			
					Found (%)	Molecular formula	Calc. (%)
2	[128]	–	–	C	33.7	$C_8H_4F_8O_2$	33.8
				H	1.5		1.4
				F	53.9		53.5
3	125	1.650	1.325	C	31.2	$C_8H_4F_{10}O$	31.4
				H	1.3		1.3
				F	61.9		62.1
5	[64]	–	–	C	29.2	$C_8H_4F_{12}$	29.3
				H	1.2		1.2
				F	68.7		69.5
7	209 (dec.)	1.715	1.374	C	36.0	$C_9H_6F_8O_2$	36.3
				H	2.0		2.0
				F	50.6		51.0
9	145	1.615	1.337	C	33.6	$C_9H_6F_{10}O$	33.8
				H	1.7		1.9
				F	59.2		59.4
10	[85]	–	–	C	36.3	$C_9H_6F_8O_2$	36.3
				H	1.9		2.0
				F	50.6		51.0
11	[171] H_2O	–	–	C	36.3	$C_9H_8F_6O_4$	36.8
				H	2.6		2.7
				F	38.7		38.8
13	[178] bzl.	–	–	F	41.3	$C_9H_7F_6NO_2$	41.4
				N	5.2		5.1

Table 3
NMR data of compounds prepared

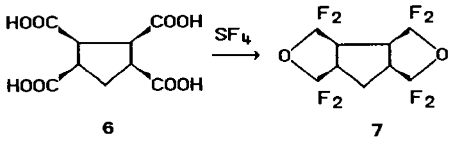
Formula	Nucleus No.	Signal struct.	Chemical shift (ppm)	Coupling constants (Hz)
 **2**	1	AB	−60.75	$^{2}J_{1,2} = 146.9$
	2	AB	−80.60	$^{2}J_{2,1} = 146.9$
 **3**	1	bs	−67.88	
	2	bd	−63.08	$^{3}J_{2,3} = 140$
	3	bd	−81.72	$^{3}J_{3,2} = 140$
 **5**	1	dt	−72.21	$^{3}J_{1,2} = 6.8$ $^{4}J_{1,2} = 1.7$
	2	bs	3.77	
 **7**	1	bd	−60.00	$^{2}J_{1,2} = 144$
	2	bd	−78.49	$^{2}J_{2,1} = 144$
	3	bd	−61.43	$^{2}J_{3,4} = 153$
	4	bd	−71.88	$^{2}J_{4,3} = 153$
 **9**	1	bs	−70.54	
	2	bd	−63.28	$^{2}J_{2,3} = 147$
	3	bd	−72.81	$^{2}J_{3,2} = 147$
 **10**	1	bd	−76.86	$^{2}J_{1,2} = 152$
	2	bd	−69.63	$^{2}J_{2,1} = 152$
	3	dm	−58.87	$^{2}J_{3,4} = 147$
	4	dm	−76.44	$^{2}J_{4,3} = 147$
 **11**	1	d	−70.35	$^{3}J_{1,2} = 8.8$
 **12**	1	d	−66.91	$^{3}J_{1,3} = 8.7$
	2	d	−69.57	$^{3}J_{2,4} = 8.4$
 **13**	1	d	−70.10	$^{3}J_{1,2} = 8.5$



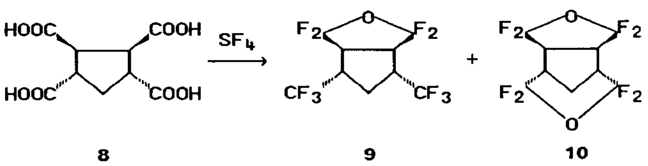
Scheme 1.



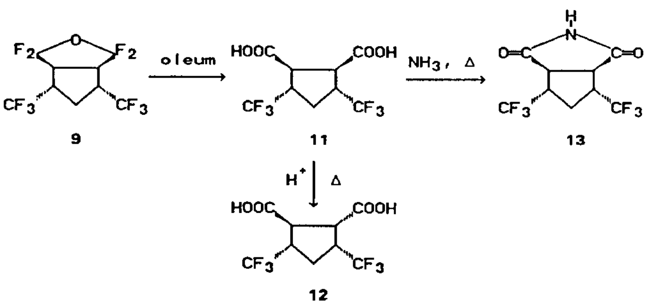
Scheme 2.



Scheme 3.



Scheme 4.



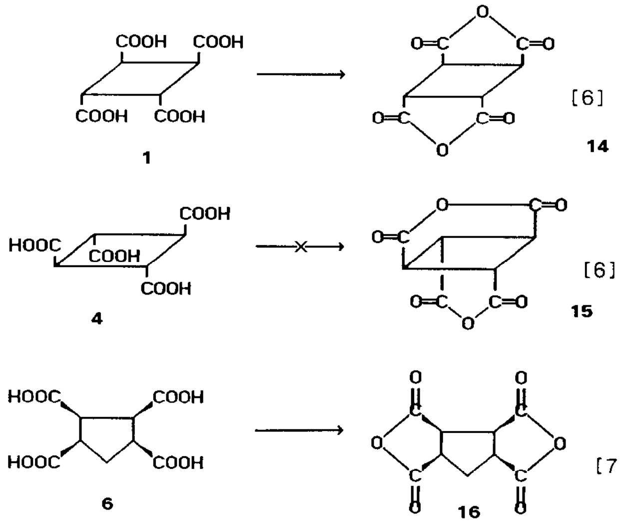
Scheme 5.

temperatures (90 °C) gave only the fully fluorinated product, *trans,trans,trans*-1,2,3,4-tetrakis(trifluoro-methyl)cyclobutane (**5**) (Scheme 2), but no products of 1,3-cyclization or bicyclic and tricyclic ethers were observed.

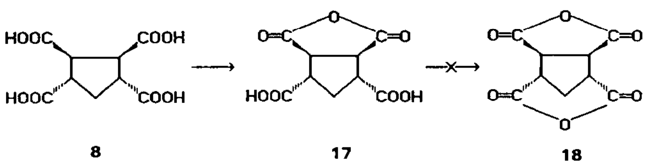
Fluorination of *cis,cis,cis*-1,2,3,4-cyclopentanetetracarboxylic acid (**6**) with SF_4 at 115 °C yielded the tricyclic diether **7** as the sole product (Scheme 3).

Fluorination of *trans,cis,trans*-1,2,3,4-cyclopentanetetracarboxylic acid (**8**) with SF_4 at 115 °C yielded the bicyclic ether **9** as the major product together with small amounts of the tricyclic diether **10** (Scheme 4).

The structure of bicyclic ether **9** has been demonstrated by NMR spectroscopy and by acid hydrolysis (oleum) to the corresponding dicarboxylic acid **11**. The latter was converted to the *trans* isomer **12** and to the cyclic imide **13** (Scheme 5).



Scheme 6.



Scheme 7.

The possibility of the formation of bicyclic and tricyclic ethers is in agreement with known information that cyclobutane- and cyclopentane-polycarboxylic acids form (or do not form) corresponding polycyclic anhydrides as listed in Scheme 6.

However, in the case of *trans,cis,trans*-1,2,3,4-cyclopentanetetracarboxylic acid (**8**) only the monoanhydride **17**, but not the dianhydride **18**, was obtained [7] (Scheme 7).

It should be noted that the formation of the tricyclic ether **10** is the first recorded example of the 1,3-cyclization of cyclic alkanepolycarboxylic acids during fluorination with SF_4.

References

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